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Some Aspects of the Lattice Destruction of Polyethylene Due to Electron Irradiation

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When $n\text{-C}_{28}\text{H}_{58}$ is exposed to electron beams, the (200) and (110) spacings remain constant independently of irradiation dose, and for the longer paraffins, these spacings increase with the dose. The longer the molecules, the more remarkable their dose dependence is. Polyethylenes are more easily subjected to electron radiation damage than $n\text{-C}_{94}\text{H}_{190}$, although the length of stem segments of both crystals is the same. The difference is caused by that of the crystalline state between them; polyethylene crystals are composed of folded chains, while molecules are extended in $n\text{-C}_{94}\text{H}_{194}$. The fact that the irradiation behavior depends on the molecular length is interpreted in terms of molecular mobility within the crystal lattice. Since in the case of paraffins with small length, molecules are very mobile, the lattice strain imposed by electron irradiation is relaxed and apparently the lattice spacings are less dependent on the irradiation dose. Further, the mechanism of lattice destruction of polyethylene is examined using the optical transform method; model lattices are set up and its optical transforms are compared with the electron diffraction patterns. It is found that the cross-link model proposed by Nagasawa and Kobayashi is not suitable as it is.

KEY WORDS: Polyethylene/ Paraffin/ Radiation damage/ Cross-link/
Optical transform/

INTRODUCTION

The radiation damage of polymer crystals due to electron beams is investigated very well in relation to electron microscopy.¹⁾ Above all, polyethylenes have been extensively studied in various aspects of the radiation damage, for example, the effects of temperatures, accelerating voltage etc.,²⁻⁶⁾ because they are rather resistant to radiation damage and well-formed single crystals are easily prepared. Since paraffins are well-defined with regard to their chemical and crystallographical structures, they have extensively examined as a model substance of polyethylene to compare their irradiation behavior with that of polyethylene.^{7,8)} The irradiation behavior of these substances has been phenomenally made clear; the lattice spacings of polyethylene crystals increase with radiation dose while those of paraffins are less dependent on it, the phase transition is induced in paraffins by electron irradiation,^{9,10)} in shorter paraffins amorphous patches are segregated out of the crystal lattice in the process of electron radiation damage.^{11,12)} In the case of paraffins, these radiation-induced changes in the crystalline state have been found to be related closely with the molecular mobility in the crystal lattice. Full understanding of these phenomena, however,

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is not attained, partly because it is not known what chemical changes occur in the crystal lattice by electron irradiation. For the damage mechanism of polyethylene due to electron radiation, the formation of cross-link was first proposed by Nagasawa and Kobayashi¹³⁾ and this model was modified by Guiu and Shadrake.¹⁴⁾ Here, by the analogy of optical transforms of two-dimensional lattices to the electron diffraction patterns, the mechanism of lattice destruction was examined and discussed mainly on the basis of this model.

EXPERIMENTAL

The following materials were used; *n*-paraffins *n*-C₂₈H₅₈, *n*-C₃₅H₇₂ and *n*-C₄₄H₉₀ which are commercially available, *n*-C₉₄H₁₉₀ which is offered by the courtesy of Dr. R.K. Eby, NBS, unfractionated linear polyethylene Sholex 6050 produced by Showa Denko K.K. and fractionated one which is commercially available as produced by NBS. Thereafter, these paraffins are abbreviated to *n*-C₂₈, *n*-C₃₅, *n*-C₄₄ and *n*-C₉₄. *n*-Paraffin *n*-C₂₈ was crystallized from 0.1% solution in ethanol, *n*-C₃₅ and *n*-C₄₄ in *n*-heptane and *n*-C₉₄ in *p*-xylene. Polyethylene single crystals were prepared by isothermal crystallization at 80°C from 0.05% solution in *p*-xylene.

Drawn polyethylene thin films were also examined and these were prepared as follows. A drop of rather concentrated hot solution (about 1%) in *p*-xylene was casted onto a surface of hot water at a temperature just below its boiling point. Then, the solution quickly spread on the surface. After evaporation of the solvent, a polyethylene thin film was left there. This film was quickly drawn on the surface with tweezers before cooling and subsequently picked up on a copper grid for electron microscopy.

Radiation damage of these specimens due to electron bombardment was measured from the change of electron diffraction patterns using a 500 kV electron microscope, JEM 500, as reported previously.¹⁰⁾ Morphological observations were carried out with a 100 kV conventional electron microscope, JEM 7A.

In order to examine the structural changes of polyethylene lattice in the process of damage, a simulation method was adopted using the optical transform technique; two-dimensional lattice models were assumed and their optical transforms were compared with real electron diffraction patterns. Two-dimensional lattice models were drawn using an X-Y plotter controlled with an electronic microcomputer. These drawings were photographically reduced into patterns of 5 mm × 5 mm in size on photographic films. Using these films themselves as masks, their optical transforms were obtained with a technique developed by Lipson and Taylor.¹⁵⁾

RESULTS

A series of photographs in Fig. 1 shows the change of electron diffraction patterns of a polyethylene single crystal due to electron irradiation. The diffraction pattern is a typical N-pattern at an exposure of rather low dose. Diffraction spots become broadened with increasing exposure time and successively fade away beginning

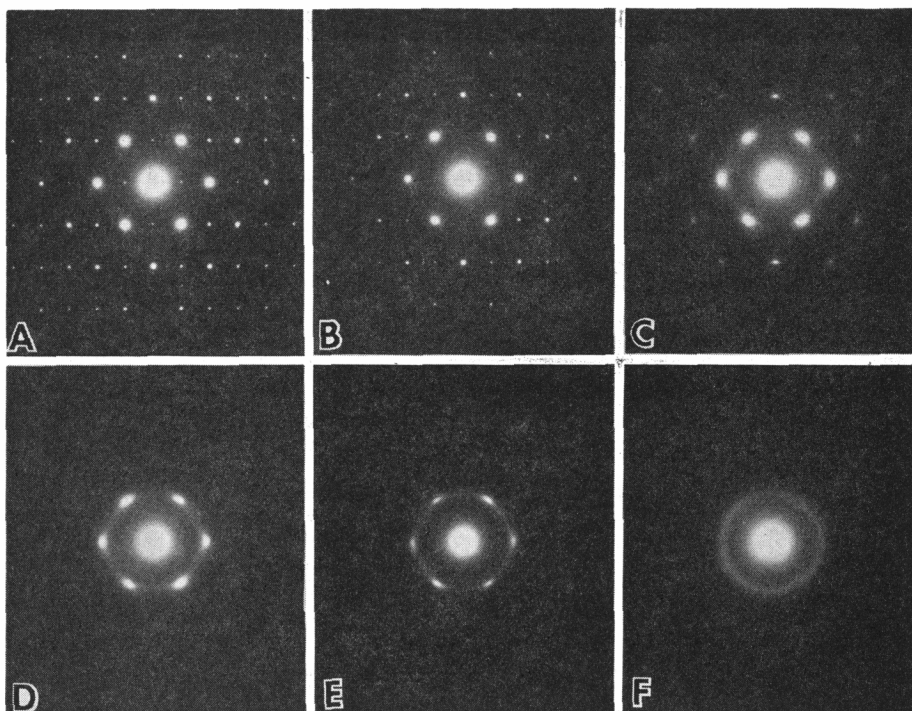


Fig. 1. The electron diffraction patterns of polyethylene single crystals after an exposure of (A) 0.06×10^{-2} , (B) 0.54×10^{-2} , (C) 1.02×10^{-2} , (D) 1.75×10^{-2} , (E) 1.98×10^{-2} and over 2.0×10^{-2} C/cm².

with the higher order spots. The diffraction pattern itself eventually transfers into a halo for a prolonged exposure over 2×10^{-2} C/cm². This indicates that crystals become disordered or distorted more and more with increasing radiation dose and deteriorate into an amorphism. In the case of drawn polyethylene films, spotty diffractions of initial fiber patterns gradually broadened and arced with electron irradiation. From this change in fiber pattern, it is considered that molecular chains, which are parallelly arranged to the fiber axis in original specimens, become disordered and inclined with respect to the axis during the progress of radiation damage.

As electron diffraction patterns become blurred with electron irradiation, the lattice spacings change. The dependence of (110) and (200) lattice spacings of paraffins and polyethylene single crystals on the radiation dose is shown in Fig. 2 and that of (002) one of drawn polyethylenes in Fig. 3. Though it is crystallographically preferable to measure the change of (020) spacing, the 020 reflection becomes unobservable because of its low intensity at a much earlier stage of irradiation before the merge of (110) and (200) spacings takes place. It is seen from Fig. 2 that the (110) and (200) spacings are almost independent of the irradiation dose in the case of paraffins of short length, e.g. n -C₂₈. As the chain length becomes longer, the dose dependence of lattice spacing is appreciable. The dependence of the (200) spacing is more marked. When polyethylene single crystals are irradiated at a exposure of 2×10^{-2} C/cm², the (110) and (200) spacings merge and crystals degenerate into an

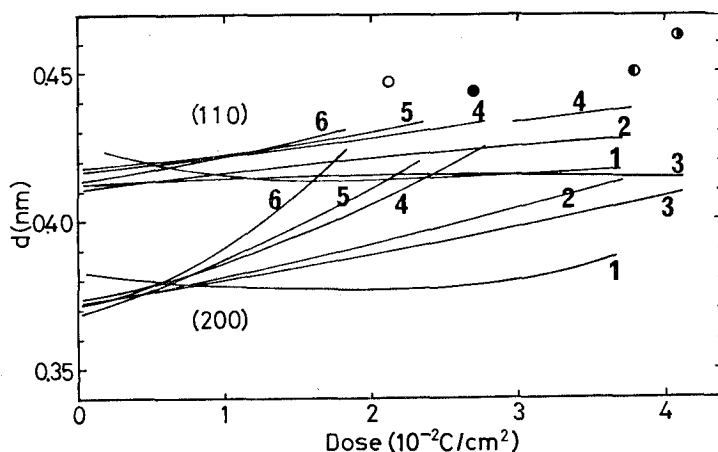


Fig. 2. The lattice spacings of (110) and (200) of various paraffins and polyethylenes as a function of radiation dose; (1) $n\text{-C}_{28}\text{H}_{58}$, (2) $n\text{-C}_{35}\text{H}_{72}$, (3) $n\text{-C}_{33}\text{H}_{90}$, (4) $n\text{-C}_{33}\text{H}_{190}$, (5) unfractionated polyethylene Sholex 6050 and (6) fractionated one (SRM-1483, $M_w=32100$). Following marks show the spacing corresponding to the amorphous halo: \bullet $n\text{-C}_{35}\text{H}_{72}$, \circ $n\text{-C}_{44}\text{H}_{90}$, \circ Sholex 6050 and \bullet SRM-1483.

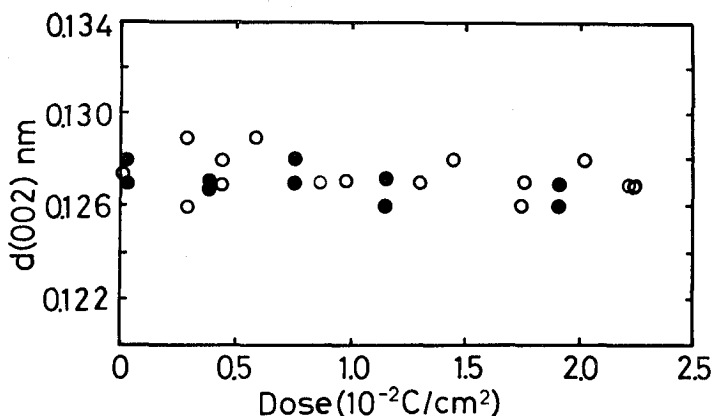


Fig. 3. The (002) lattice spacing of a drawn polyethylene (Sholex 6050) as a function of radiation dose; \bullet as-drawn and \circ annealed at 125°C for 12 hrs.

amorphous state. This irradiation dose is called a total end point dose. The total end point dose of $n\text{-C}_{94}$ is noticeably larger than that of polyethylenes. In other words, polyethylene crystals are damaged more heavily than those of $n\text{-C}_{94}$, although the thickness of the former (about 13 nm) is comparable to that of the latter which is equal to the molecular length, 12.2 nm.

Figure 3 shows that the (002) spacing of drawn polyethylenes slightly decreases with an increase of the dose. There is an observation by X-ray diffraction method that the (002) lattice spacing of irradiated polyethylene single crystals increases by a extremely small amount at a moderate electron irradiation.¹⁶⁾ However, their irradiation behavior is inferred to be very similar to that of drawn polyethylene

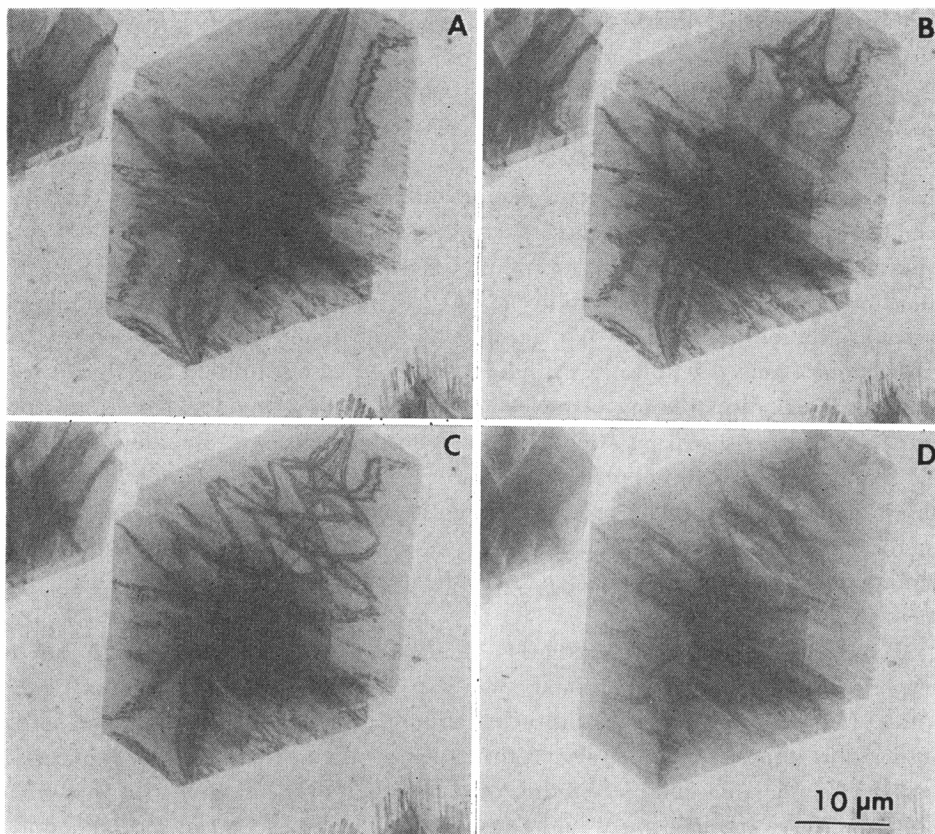


Fig. 4. The change of diffraction contrast during the electron irradiation. The radiation dose increases in the alphabetical order.

within the experimental error. The increase of the (110) and (200) spacings more than offsets the decrease of the (002) spacing. Resultingly, the unit cell expands with the radiation dose, especially in the direction of **a**-axis.

Figure 4 shows how the structure of $n\text{-C}_{44}$ paraffin crystals varies in the process of irradiation. The stripes move about through the entire crystal changing their locations and appearances drastically. These stripes arise from the diffraction contrast due to the Bragg's reflections. This change shows that the molecular orientation varies drastically from place to place during electron irradiation. In the case of polyethylene single crystals, striations running parallelly to $\langle 310 \rangle$ direction are very often observed. These do not behave in a similar way but only disappear without moving from their initial position as the radiation damage proceeds.

DISCUSSION

It is well known that molecular chains of polyethylene and paraffins suffer from chemical changes such as cross-linking, formation of double bonds, scission of bonds etc. due to electron irradiation.¹⁷⁾ When these irregularities of chemical structures are introduced into a crystal, they should work as lattice defects so that the crystal

lattice is disordered or distorted within some range around them. For example, the lattice expansion in Fig. 2 clearly results from the introduction of defects. It is not known whether or not the kind and the distribution of molecular irregularities thus formed differ between paraffins and polyethylenes. As the energy of 500 kV electrons much exceeds the energy necessary for activating these chemical reactions, however, it is justifiably assumed that these changes occur independently of the chemical, crystallographical structures of these substances and evenly throughout the crystal. In paraffins with various crystal forms, the phase transition, for example, from the monoclinic form to the orthorhombic in $n\text{-C}_{36}$, is induced when they are subject to electron radiation damage.¹⁰⁾ To accomodate the strain energy caused by the introduction of defects within the crystal lattice, the phase transition takes place with the translational displacement of molecular chains in the direction parallel to their axes. In some cases, the translational motion is accompanied with the rotation around molecular axes, i.e. a flip-flop motion, in the transition of the triclinic form to the orthorhombic in $n\text{-C}_{22}$. The protean change of meandering stripes in Fig. 4 shows that the molecular orientation varies from place to place during irradiation. This orientational change of molecular chains is the evidence of the mobility of molecules in crystals.

Thus, the dependence of radiation damage on the molecular length can be interpreted in terms of the molecular mobility. When defects are produced within crystals, the lattice disorder or distortion around them is inevitable. The lattice disorder thus imposed may be relaxed through sweep-out of defects from the interior of crystal or the molecular re-organization which is motivated by the molecular mobility. These mechanisms would be promoted by the excited molecular motions which are caused by the thermal spike originating from collisions between electrons and atoms in the lattice and by the liberation of heat associated with chemical changes. The segregation of amorphous patches in short paraffins out of the crystalline lattice^{11,12)} suggests the presence of the sweep-out mechanism. Naturally, the longer the molecular chain is, the more restricted the molecular motions are. As a consequence of the constrained mobility, the recovery of the strained lattice of longer molecules is more or less restricted and the dose dependence of lattice spacings on the molecular length results. The difference of irradiation behavior between $n\text{-C}_{94}$ and polyethylene single crystals provides decisive evidence for the difference in mobility. There is an obvious dissimilarity between their structures: stem segments of polyethylene single crystals are linked with one another by folds at the surface, while paraffin molecules have no connection with their neighbors by chemical bonds. In polyethylene composed of folded chains, stems cannot displace solely since they are connected with adjacent stem segments by the folds along the contour length of the molecule and also cannot rotate since they are anchored by the folds at the surface. The stems thus restrained are much less mobile than chains of $n\text{-C}_{94}$ and resultingly the strained lattice hardly relaxes. In this way, the dose dependence of the lattice spacings in Fig. 2 is explained on the basis of the difference of the molecular mobility among crystals. That is, the irradiation behavior should be interpreted in terms of the introduction of defects into the crystal followed by the relaxation of the strained

lattice. This is supported by the fact that even in irradiated polyethylenes, the lattice spacings are contracted once the specimens are annealed at temperatures where molecular motions are activated.¹⁶⁾

From the radiation-induced transition of paraffins, it is found that at an exposure of 1.5×10^{-3} C/cm², one defect is introduced in 500 CH₂ units on an average. On the basis of this number and the total end point dose of polyethylene, the number of defects which is needed to convert polyethylene crystals into an amorphism is estimated at one defect per about 50 CH₂ units, i.e. two defects in one stem segment.

Up to this point, the kind of structural irregularities produced by the electron irradiation and the nature of the resulting defects are not inquired into. In order to explain the lattice distortion of polyethylenes, Nagasawa and Kobayashi have first proposed the cross-link model whose essence exists in the analogy between the distortion of stems due to cross-linking and the bending of a fine beam.¹³⁾ This model was extensively studied and modified by Guiu and Shadrake¹⁴⁾ (see Fig. 5). They have applied the theory of elasticity to this model and analytically derived the strain field around a cross-link. Information on the lattice distortion can be experimentally obtained by the profile analysis of diffraction patterns. The (hk0) electron diffraction pattern is suitable for this purpose. Especially, diffuse scatterings streaking from the Bragg's spots, which convey information on the lattice distortion, are of first importance. It is difficult, however, to evaluate accurately the diffraction intensities, because the intensities are changing from time to time during exposure to electrons and multiple scatterings cannot be negligible. Hence, it is not always practical to study the lattice distortion by a straightforward analysis of the electron diffraction pattern.

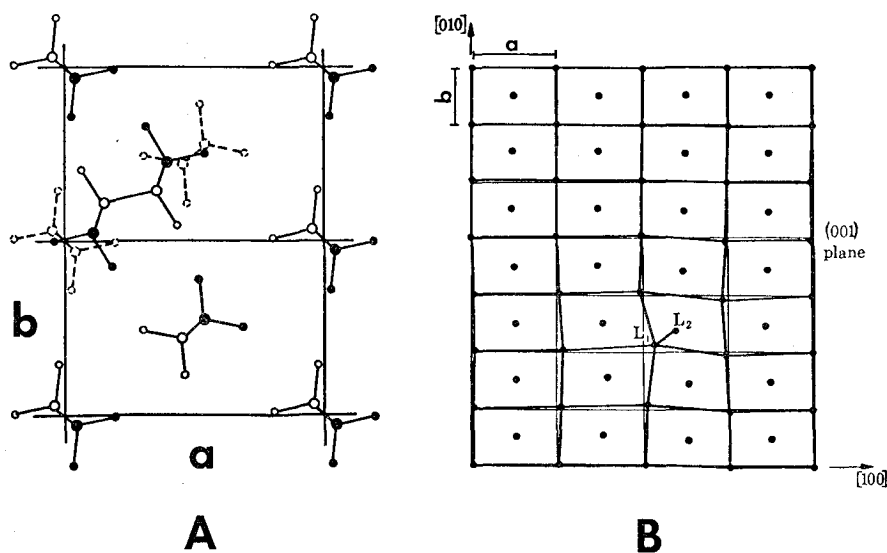


Fig. 5. The cross-link model of the lattice destruction of polyethylene. (A) the molecular conformation of the cross-link model projected on the (001) plane of the unit cell and (B) the displacements of stem segments in the (001) plane around the cross-link. The line L1-L2 denotes the cross-link (Guieu and Shadrake (14)).

Figure 6A shows a two-dimensional model lattice of the perfect polyethylene lattice, which is projected on the (001) plane. Now, the cross-link model in Fig. 5 is adopted as a defect and defects are introduced in the following way. The position for a cross-link to be introduced is determined on the basis of random numbers and the displacements of stem segments around it are calculated according to the equation by Guiu and Shadrake. Subsequently, a new model lattice is set up by adding displacements thus obtained to the positions of corresponding stems before the introduction of the defect. Here, it is assumed that the equation holds regardless of the state of the lattice, that is, whether the lattice is distorted or not. This process is

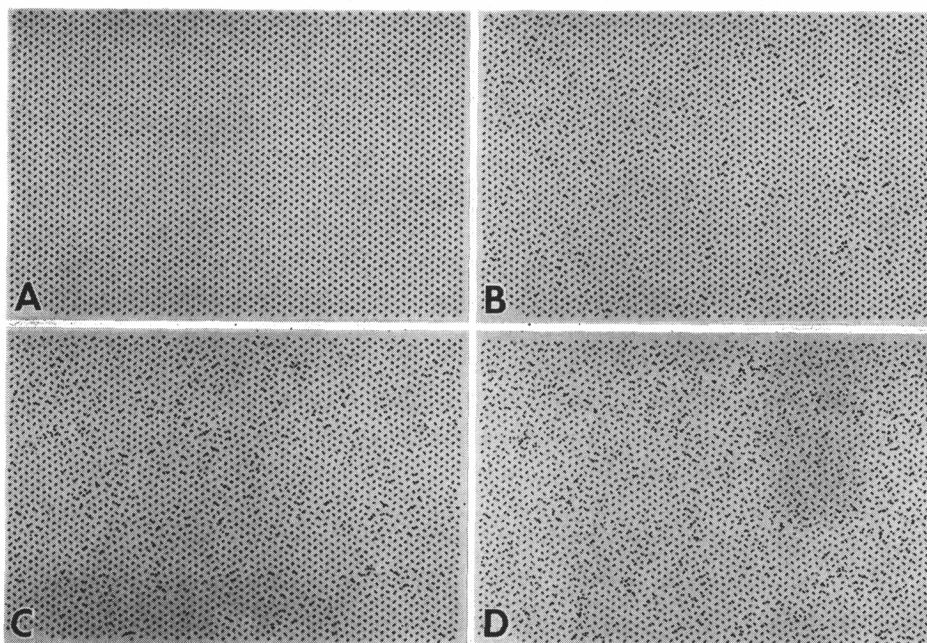


Fig. 6. Two-dimensional model lattices containing the defects due to cross-link; (A) 0, (B) 200, (C) 400 and (D) 800 defects. Dots in the models show the projections of C-C units on the (001) plane. Precisely, each spot consists of smaller two dots linked as a pair of dumbbells so that the 2_1 symmetry of operation parallel to the **a** and **b** axes is introduced in the non-damaged lattice. The **a** and **b** axes are horizontal and vertical in these figures, respectively. Hydrogen atoms are omitted out of these models.

iterated with an electronic computer and Figs. 6B, C and D show model lattices containing 200, 400 and 800 defects, respectively. These figures are formed of 40×40 unit cells. Their size is selected to correspond to a real crystallite size of polyethylene single crystals, which is measured from the line profile analysis of X-ray diffraction pattern. Figure 7 shows the corresponding optical transforms of model lattices of Fig. 6.

From the above optical simulation, we can clearly see the process that the diffraction pattern becomes broad and blurred as the ordering of the crystal lattice deteriorates. Figure 8 shows two comparable diffraction patterns: an optical diffraction pattern of the model lattice containing one defect per four CH units (Fig. 7C)

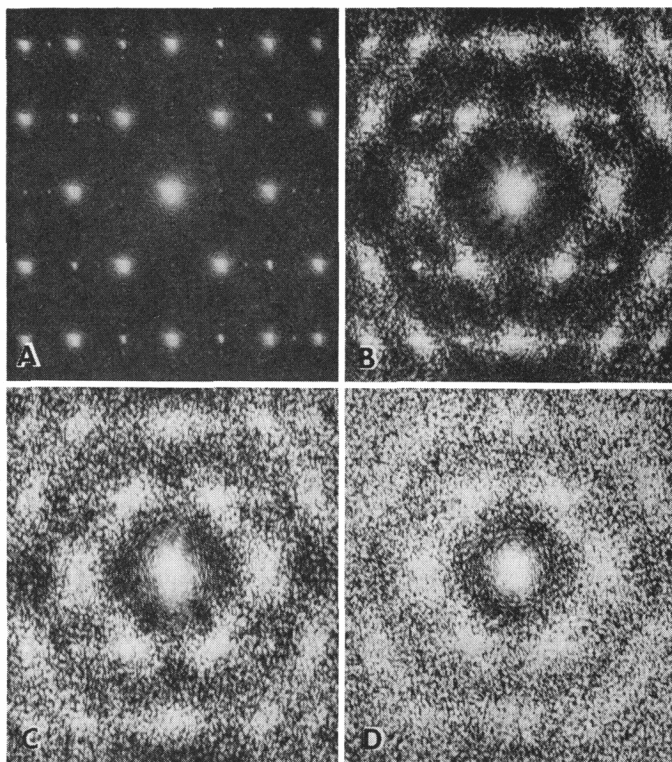


Fig. 7. Optical transforms A, B, C and D are obtained from the model lattices of Figs. 6 A, B, C and D, respectively.

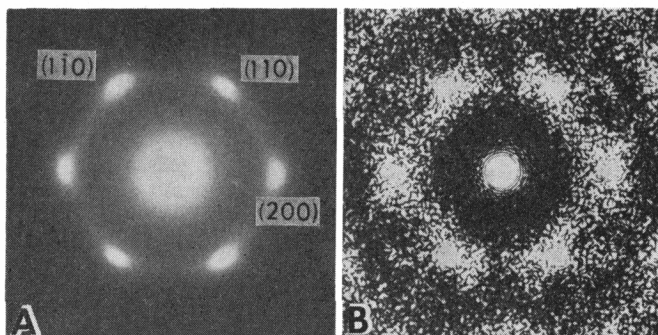


Fig. 8. The two comparable electron and optical diffraction patterns; (A) the electron diffraction pattern of polyethylene single crystal after an exposure over 1.05×10^{-2} C/cm and (B) an optical diffraction pattern of the model lattice containing one cross-link per four CH units.

and an electron diffraction pattern where the content of defects is estimated at one per a stem in such a way as described above. The diffuse scattering running from the (110) spot to the (1 $\bar{1}$ 0) one or from (110) to (200) appears quite similarly for both patterns. This similarity seems to ensure that the present scheme of disordering of the lattice represents quite well the radiation damage due to electron bombardment.

However, it is worth noting that the diffraction peaks of optical transforms do not shift till the pattern become an amorphous halo: the average lattice spacings do not change even if the model lattice is heavily disordered. This simulation does not account for the fact that the polyethylene lattice expands with an increase in the lattice distortion.

The following assumptions are used for the above simulation; (1) only two-dimensional distortion of the (001) section is taken into account and (2) the equation derived for an infinitely extended perfect crystal is used in order to calculate the displacement of stems. These assumptions do not correctly represent the mechanism of the lattice destruction of real crystals in the following bases. Firstly, as a real crystal is disordered three-dimensionally around defects, the projection of a three dimensionally distorted model lattice on the (001) plane must be involved in the construction of disordered model lattices. Unfortunately, only the two-dimensional strain field of the (001) plane is analytically available. Secondly, real crystals are bounded at the fold surface in the direction parallel to molecular axes and also are finite in size in the direction perpendicular to their axes. Moreover, molecular chains tilt at the crystal surface with irradiation. The above cross-link model itself, however, is somewhat problematic as it substantially involves only inward displacements. This disordering is essentially analogous to that due to the introduction of a vacancy into a crystal lattice. When a vacancy is introduced within a finite crystal lattice, the volume contracts because of surface effect and resultingly the lattice spacings decrease.¹⁸⁾ In this sense, it is concluded at least the cross-link model as shown in Fig. 5 does not give rise to the dilatation of crystal. From a macroscopic measurement of damaged mats of single crystals, the density is really shown to decrease with radiation dose (although it slightly increases at an initial stage of irradiation because of the collapse of voids within them or the structural changes of interlamellar regions.^{16,19)} It is also ascertained that the area of a single crystal of polyethylene increases during the observation under the microscope.²⁰⁾ These facts clearly show that the lattice expansion results from the substantial dilatation of the crystal itself. From this point of view, the destruction mechanism in which stems displace outward leading to the dilatation of the crystal must be taken into account; for instance, such bulky structural irregularities as chain kinks acting as interstitials are produced within the crystal and cause the molecular twisting.

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